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## XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-  
POUNDS.

BY C. LORING JACKSON.

Presented, June 14th, 1876.

## INTRODUCTION.

THE existence of the benzyl compounds was first established by Cannizaro,\* in 1853; for, although Liebig and Wöhler,† in their classical research on the benzoyl compounds, obtained benzylalcohol as a secondary product from the action of potassic hydrate on benzaldehyd, they merely spoke of it as an oily liquid, and did not determine its composition or properties. It was also Cannizaro ‡ who, in 1855, showed that toluol, when treated with chlorine, yielded a substance identical with the benzylchloride prepared from benzylalcohol by means of hydrochloric acid. The nature of the action of chlorine on toluol was not, however, thoroughly understood until Beilstein and Geitner,§ in 1866, found that chlorine converted cold toluol into chlor-toluol, while, with boiling toluol, it yielded benzylchloride. In the same paper, they predicted that pure chlorbenzylchloride could be prepared by the action of chlorine, either on hot chlor-toluol or on cold benzylchloride. Both these methods were tried successfully by Neuhof || in the same year, but the chlorbenzylchloride thus obtained was not the first substituted benzyl compound known, as Beilstein ¶ had already obtained the chlorbenzylmercaptan, and Naquet\*\* the chlorbenzylethylether, from the mixture of dichlortoluols, made by acting upon toluol

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\* Ann. Chem. Pharm., 88, p. 129.

† Ib., 3, p. 249.

‡ Ib., 96, p. 246.

§ Beilstein and Geitner, Ann. Chem. Pharm., 139, p. 331.

|| Neuhof, Zeitschr. der Chem., '66, p. 653.

¶ Beilstein, Ann. Chem. Pharm., 116, p. 346.

\*\* Naquet, ib., Sup. 2, p. 250. Comptes Rend., 56, p. 129.

with chlorine. Immediately after the preparation of the pure chlorbenzylchloride by Neuhof, many of its derivatives were studied by Beilstein and Kuhlberg and Neuhof,\* and the two former extended their investigations to the chlorbenzyl compounds containing more than one atom of chlorine attached to the benzole ring. Since that time, but little attention has been given to this class of compounds; the only researches being those of Böhler,† and later, Vogt and Henninger,‡ on the sulphoacids, of Berlin,§ who obtained some curious results from the amines, and of Sintenis,|| who investigated the ethers.

Beside these chlorbenzyl compounds, only two other classes of substances lying within the range of this paper have been studied, the nitrobenzyl compounds, — the first of which, nitrobenzylchloride, was described by Beilstein and Geitner in 1866, in the paper already referred to; ¶ its derivatives were further studied by Grimaux,\*\* Beilstein, and Kuhlberg,†† Böhler,‡‡ Strakosch,§§ Czumpelik,||| Radziszewski,¶¶ Henry,\*\*\* and Jackson; ††† and a few amidobenzyl compounds, the cyanide prepared by Czumpelik,‡‡‡ and the amines by Strakosch. §§§

All these substances belonged to the para series, and no isomeric chlor- or nitrobenzyl compounds were known with the exception, perhaps, of the monochlorbenzylsulphosalts described by Vogt and Henninger, |||| and the isomeric nitrobenzylalcohol obtained by Gri-

\* Beilstein, Kuhlberg, Neuhof, *Ann. Chem. Pharm.*, 147, p. 339; *ib.*, 150, p. 286; *ib.*, 146, p. 319.

† Böhler, *Zeitschr. Chem.*, 1868, p. 440.

‡ Vogt, Henninger, *Ann. Chim. Phys.* [4], 27, p. 130; *Ann. Chem. Pharm.*, 165, p. 362.

§ Berlin, *Ann. Chem. Pharm.*, 151, p. 137.

|| Sintenis, *ib.*, 161, p. 329.

¶ Beilstein and Geitner, *Ann. Chem. Pharm.*, 139, p. 331.

\*\* Grimaux, *Comptes Rend.*, LXV., p. 211; *Ann. Chem. Pharm.*, 145, p. 46.

†† Beilstein, Kuhlberg, Neuhof, *Ann. Chem. Pharm.*, 147, p. 339; *ib.*, 150, p. 286; *ib.*, 146, p. 319.

‡‡ Böhler, *Zeitschr. Chem.*, 1868, p. 440.

§§ Strakosch, *Ber. D. Ch. G.*, 1872, p. 692.

||| Czumpelik, *ib.*, 1870, p. 473.

¶¶ Radziszewski, *ib.*, 1870, p. 198.

\*\*\* Henry, *ib.*, 1869, p. 637.

††† Jackson, *ib.*, 1875, p. 321.

‡‡‡ Czumpelik, *ib.*, 1870, p. 473.

§§§ Strakosch, *ib.*, 1872, p. 692.

|||| Vogt, Henninger, *Ann. Chim. Phys.* [4], 27, p. 130; *Ann. Chem. Pharm.*, 165, p. 362.

maux\* from nitrobenzaldehyd, until Wachendorff,† in 1875, described the orthonitrobenzylbromide and chloride. Soon after, in a preliminary notice‡ of a portion of the work contained in these papers, the para- meta- and orthobrombenzylbromides were described; finally, in 1877, Wachendorff published a very interesting paper § upon the nitrobenzylchlorides and bromides, in which he described the metanitrobenzylbromide, and called attention to the striking fact that metanitrobenzylchloride could not be obtained under conditions which gave without difficulty the paranitrobenzylchloride, while he had not as yet succeeded in obtaining the orthonitrobenzylbromide under the conditions which furnished both of its isomeres; he said, however, that he did not despair of obtaining it by new experiments under different conditions; from this it would seem probable that the statements made in his preliminary notice in regard to orthonitrobenzylchloride and bromide, have been proved incorrect by his later experiments.

The object of these papers is to add to our knowledge of this little studied class of compounds, and, also, to make some comparisons between the replaceability of the haloid atoms in the side-chain, which it is hoped may in the future throw some light upon the nature of chemical attraction. The substituted benzylbromides have been used as the starting-point for each class of compounds, because these substances can be easily obtained by the action of weighed amounts of bromine upon the corresponding substituted toluols in the state of vapor. This action of bromine on boiling toluol was first studied by Lauth and Grimaux,|| Cannizaro,¶ and Beilstein,\*\* who proved that the substance thus formed was identical with the benzylbromide previously obtained by Kekule †† from benzylalcohol by means of hydrobromic acid.

## FIRST PAPER.

### ON CERTAIN SUBSTITUTED BENZYL BROMIDES.

C. LORING JACKSON.

*Parabrombenzylbromide* ( $C_6H_4Br^P.CH_2Br$ ). — Preparation. First Method. Ten grammes of pure parabromtoluol, melting-point  $28.5^\circ$ ,

\* Grimaux, Comptes Rend., LXV., p. 211; Ann. Chem. Pharm., 145, p. 46.

† Wachendorff, Ber. D. Ch. G., 1875, p. 1101.

‡ Jackson, ib., 1876, p. 931.

§ Wachendorff, Ann. Chem. Pharm., 185, p. 259.

|| Lauth and Grimaux, Bull. Soc. Chim. [2], VII., p. 108.

¶ Cannizaro, Ann. Chem. Pharm., 141, p. 198.

\*\* Beilstein, ib., 143, p. 369.

†† Kekule, Ann. Chem. Pharm., 137, p. 188.